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The Pore Diameters of Osmotic
Membranes.

II.

The Permeability of Porcelain and Copper
Ferrocyanide Membranes.

A THESIS

SUBMITTED TO THE FACULTY OF THE DEPARTMENT OF
LITERATURE, SCIENCE, AND THE ARTS OF THE
UNIVERSITY OF MICHIGAN FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY.

By FLOYD E. BARTELL.

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PORE DIAMETERS OF OSMOTIC MEMBRANES

BY F. E. BARTELL

The fact that some grades of porcelain act "osmotically" was clearly demonstrated by Graham.¹ He made use of a porcelain cylinder of about 170 cc capacity, to which was attached an outlet tube, calibrated in mm, for measuring the change of height of the solution. This apparatus was filled with the solution to be tested, then placed in a jar of distilled water the temperature of which was held between 56° and 64° Fahr. Some of the results obtained are as follows: A solution containing 1 percent of Rochelle salt produced a rise in the column of 82 mm; phosphoric acid of the same strength, gave 62 mm; sugar and other organic substances gave something less than 20 mm.

Notwithstanding the fact that certain grades of porcelain do produce osmotic effects when tested, it is also true that most grades of porcelain do not produce apparent osmotic effects. The difference in the behavior of the porcelain consequently raises the following questions: What is characteristic of that porcelain which is capable of producing osmosis? Is the *composition* of the porcelain or the *internal structure* the principal factor, and if the latter, is there any definite relation between the size of the pores in porcelain and osmotic effects?

Relatively little attention has been given to such membranes as porcelain, marble,² etc., with which, owing to the fact that they permit much of the dissolved substance as well as the solvent to pass through, the osmotic effects are slight and the results are only qualitative. The main object of recent investigators appears to have been to determine whether or not the gas laws apply to osmotic pressure.

The purpose of this investigation is not to determine the

¹ Phil. Trans., 144, 177 (1854).

² Cean stone and marble membranes were used by Dutrochet in his investigations of osmotic phenomena (Ann. Chim. Phys., 49, 411 (1832)).

maximum osmotic pressures, then compare them with gaseous pressures; it is to study some of these relatively neglected membranes from a different point of view, to study their structure and to compare this with their ability to produce osmotic effects however small. The aim is to add a little, if possible, to our knowledge of how a membrane acts when osmotic phenomena are observed.

In a previous article¹ a brief account was given of results obtained in a study of the relation of the size of the pores in porcelain to the osmotic effects produced. The membranes investigated were porcelain, porcelain clogged with barium sulphate, and porcelain clogged with sulphur. Numerous tests have since been made with these membranes. Also, the work has been extended to include membranes of porcelain clogged with lead chromate, with lead sulphate, with copper sulphide and with copper ferrocyanide.

The object of this paper is to describe, briefly, some of the preliminary experiments which led to this investigation, to give the results obtained in recent investigations and to point out the limits of accuracy of the method and the precautions to be observed in measuring pore diameters by this method.

Preliminary Experiments

Discs cut from ordinary unglazed porcelain drying plates were sealed over the mouth of a thistle tube which was then filled with a normal sugar solution, placed in distilled water and tested for ability to give osmotic effect. These were found to give no osmotic effects. Other discs, made from battery cups and some other grades of porcelain, when tested in a similar manner, gave marked osmotic effects. These discs were then examined under the microscope and it was readily seen that the porcelain producing the osmotic effect was that with the finest texture. It seemed altogether probable that the porcelain with the finest texture was also of smallest pore diameters. It also seemed reasonable to

¹ Jour. Am. Chem. Soc., 31, 1194 (1909).

suppose that if the size of the pores makes the difference, osmotic effects should be obtained from a plate, which alone will not show osmotic effects, provided its pores be sufficiently clogged with some insoluble material. With these considerations in mind a series of experiments were undertaken.

Experiment 1.—A small porcelain disc, about 25 mm in diameter was cut from an unglazed porcelain plate and sealed, by means of marine glue, over the mouth of an ordinary thistle tube. The bulb of the tube was then filled with a normal sugar solution. The osmotic cell thus prepared, was set up in a beaker of distilled water for osmotic tests. The height of the liquid in the tube was adjusted to the same height as the water outside. Twelve hours later the solution was 5 mm below the surface of the water. After 48 hours the column had returned to practically its original position and at the end of six days had risen not more than 2 mm, a height ascribable to capillary ascension in the glass tube.

Experiment 2.—A porcelain disc made from the porcelain of fine texture previously mentioned, was treated in the same manner as the porcelain in Experiment 1, and set up for osmotic tests. At the end of 12 hours the column had risen 24 mm; at the end of 24 hours, 45 mm; at the end of 40 hours, 72 mm; at the end of 96 hours, 98 mm.

Experiment 3.—Water was forced through the porcelain disc, used in Experiment 1, to remove the sugar solution. A solution containing freshly precipitated barium sulphate, formed by treating M/2 barium chloride¹ with M/2 sodium sulphate, was forced through under pressure. This was followed by more water to remove any excess of solution remaining. The cell was then filled with M sugar solution and set up for osmotic tests as before (Experiment 1). At the end of 2 hours the column had risen 3 mm, and after 24 hours it stood at 15 mm.

Experiment 4.—Another disc, cut from the same porcelain

¹ M, is used to indicate molecular normal, being preferred to the more commonly used symbol N which occasionally leaves one in doubt whether molecular normal or equivalent normal is meant.

as the first, giving no osmotic effect in its original condition, was placed in M/2 barium chloride solution for 1 hour. It was then transferred to an M/2 sodium sulphate solution where it remained for 40 minutes. Water was forced through to remove the solutions present, then the disc was tested for osmotic effect. After standing 12 hours the column had risen 28 mm; after 24 hours it had risen 45 mm.

Experiment 5.—A solution containing a finely divided precipitate of sulphur, formed by treating a sodium thio-sulphate solution with dilute sulphuric acid, was forced through another such disc. This disc gave somewhat more marked osmotic effects than those in the preceding experiments. After 12 hours the column stood at 24 mm; after 24 hours, at 60 mm; and after 48 hours, at 85 mm.

From the above experiments it is evident that by clogging the pores of the coarse grained porcelain we can make it act "osmotically." This, then, is in favor of the view that the internal structure, or the pore diameter, is one of the main factors in determining the ability of a porcelain membrane to give osmotic effects. Let us assume that the pore diameter is the principal factor. It then follows: (1) That by clogging the pores with any insoluble precipitate, whatsoever, we should be able to make any porcelain act "osmotically." (2) That the border line between osmotic effect and no osmotic effect should be indicated by a definite pore diameter. With pore diameters larger than some maximum, no osmotic effects should be obtained; with pore diameters smaller than this maximum, osmotic effects should be obtained.

Method for Calculating Pore Diameters

The results obtained from an investigation of the permeability of porcelain membranes showed that Poiseuille's laws for the passage of liquids through capillary tubes apply to the passage of water through porcelain.¹ By making use of Poiseuille's formula $Q = \frac{KD^4PT}{L}$, (in which Q represents

¹ Jour. Phys. Chem., 15, 659 (1911).

the quantity of liquid passing through a tube of L length and D diameter in T time under P pressure), and solving for D , it is possible to estimate the diameter of the pores in a membrane. It is, however, impossible to obtain correct numerical values for L , the length of the pores, for it cannot be assumed that the pores in a membrane are arranged as straight tubes perpendicular to the faces of the membrane. The average length of the pores is probably much greater than this, therefore, we are unable to obtain anything like absolute values by this method.

The method finally adopted for measurements of pore diameters in membranes was one based upon the application of Jurin's law, which gives us a means for calculating diameters of capillary tubes, independent of their lengths. $a^2 = h r$, where r is the radius of the tube, h the height to which liquid ascends due to capillarity, and a^2 is one of the so-called capillary constants. For water at 20°C $a^2 = 14.823 \text{ mm}$. Suppose, for example, that the radius of the tube is 1 mm , then water will rise in that tube to the height of 14.823 mm . To force water out of such a tube will require the hydrostatic pressure of a column of water of this same height. Furthermore, if water fills a very short piece of capillary, of this same diameter, the same pressure will be required to force it out. By measuring the pressure required to force water out of a membrane saturated with water we can estimate the diameter of the pores in that membrane.

The applicability and accuracy of this method was demonstrated experimentally.¹ Fine glass capillaries were drawn out, filled with water, and the pressure necessary to force out this water with air was determined. Later these same tubes were measured directly under the microscope. A close agreement between the calculated and observed diameters was obtained.

It is obvious that this method is applicable only to the investigation of membranes strong enough to withstand the pressures, *i. e.*, membranes with relatively large pores. Some

¹ Jour. Am. Chem. Soc., **31**, 11 (1909).

of the porcelain discs used in this investigation burst at pressures little above ten atmospheres. In case the pores were of approximately molecular dimensions, assuming that capillary laws would apply for these diameters and also assuming 10^{-7} cm to be the order of molecular magnitudes, the pressure required to force the water out would be in the neighborhood of three thousand atmospheres (as a matter of fact the pressure would be much greater than this owing to molecular attraction). It is thus altogether improbable that the precipitation membranes capable of giving osmotic pressures comparable with those calculated from the gas laws, would withstand the pressure requisite to estimate the diameter of the pores. Pressures and corresponding pore diameters are shown in Table I.

Column I, contains the pressure (kilograms per square centimeter), calculated as necessary to force water out of capillaries with diameters given in Column III.

TABLE I

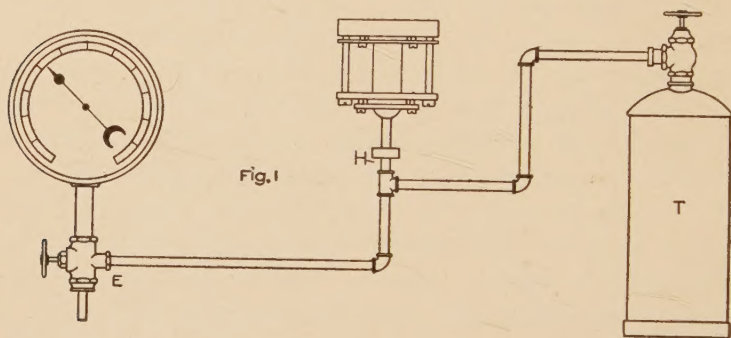
I Pressure	II Temperature	III Diameter in microns
1	20° C	2.9646
2	20° C	1.4823
5	20° C	0.5930
10	20° C	0.2964
25	20° C	0.1186
100	20° C	0.0296
1000	20° C	0.0029

Apparatus

The membranes investigated were, in most cases, different grades of unglazed porcelain. The pressure required to force water out of them was determined with an apparatus as shown in Fig. 1.

The holder containing the membrane which was to be investigated was attached at H. Pressures, applied by means of compressed air from tank T, were read directly from the pressure gauge, E. The porcelain plates were about 4 mm

in thickness and were held between washers of dermatine (DD, Fig. 2) which left exposed a surface 14 mm in diameter. The cell proper was a thick walled glass cylinder, G, 40 mm



long and 14 mm internal diameter, with ground ends which rested on washers of dermatine. The rest of the holder was of brass held together by means of screws. The holder was so constructed that the porcelain plate remained in position during the entire course of an experiment.

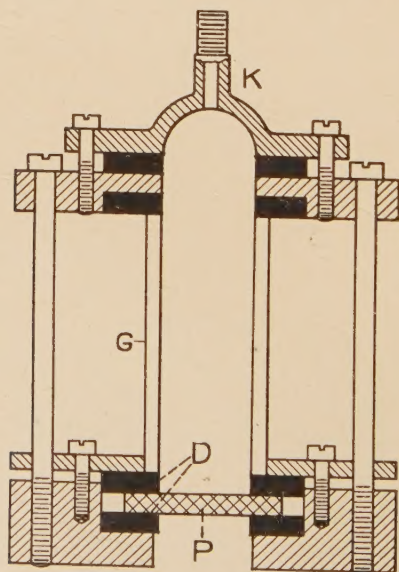


Fig. 2

When the apparatus was set up for osmotic tests the threaded outlet tube K, was replaced by a glass tube 100 mm in length and 3 mm internal diameter. This glass tube was held firmly in place by a washer of dermatine which was in turn securely fastened by a brass washer.

Method of Operation

In carrying out an experiment, the porcelain plate was fastened in place in the holder then thoroughly saturated with water. The holder was then attached to the pressure apparatus with the plate facing upward. A piece of thick plate glass was placed above this for when high pressures were employed the porcelain discs frequently burst. Gradually increasing air pressure was brought to bear on the under side of the membrane. As water was forced out of the pores, air bubbles came through; these were most readily detected by having a thin layer of water on the upper side of the plate, and watching with a lens. The pressure at which the first bubble appeared was noted, but for the calculation of the pore diameters the pressure was taken at which 100–125 bubbles came through. After the pressure required to force the water out with air had been determined, the cell was disconnected from the pressure apparatus, filled with normal sugar solution, adjusted for osmotic tests and placed in a 600 cc beaker of distilled water. The apparatus was thus converted into an "osmotic cell" experiment without disarranging disc or cylinder. The meniscus of the sugar solution within the tube was adjusted to the level of the water in the beaker. If the meniscus rose to a height greater than 5 mm (an ascension of this amount was considered to be greater than could be accounted for by capillary ascension or change in the temperature) the membrane was considered capable of producing osmotic effects. As a rule, readings were taken every 12 hours; in every case the cell was allowed to stand at least 24 hours before conclusions were drawn.

In both the pressure experiments and the osmotic tests the temperature was held close to 20° C and did not vary

more than one degree either way. Pressures were measured in kilograms per square centimeter, therefore, substituting in the formula, $D = \frac{a^2 \times 2}{P \times 10^4}$, gives the diameter of the pores in millimeters.

Measurement of Pore Diameters in Porcelain

Discs from more than 80 samples of porcelain were prepared, the pore diameter of each disc was determined, after which tests were made for osmotic effects.

The range of pressure employed from the appearance of the first bubble until so many bubbles had appeared that it was impossible to accurately count them was, in most cases, comparatively small. Pressures together with corresponding pore diameters, obtained with one sample of porcelain, are given in Table II.

TABLE II

Column I. Pressure in kilograms per square centimeter.

Column II. The diameter in microns of a capillary corresponding to the pressure.

Column III. The number of bubbles in a circle of 14 mm diameter.

I Pressure	II Diameter	III Number of bubbles
7.0	0.422	None
7.4	0.400	None
7.6	0.388	5
7.7	0.383	15
7.8	0.378	75
8.0	0.369	120
8.2	0.360	Too many to count

The calculated diameter for the five largest pores in this porcelain was 0.388 microns. The value obtained for an innumerable number was 0.360 microns. This, of course, does not exclude the possibility that there are yet more much smaller. In recording results of experiment the value 0.369 would be taken.

It was also found that, with porcelain of approximately

the same grade as that used in the preceding experiment, it was advisable to wait at least five minutes after each successive increase of pressure before making a final count of air bubbles. It takes some time to force the water out of the pores as is shown by the data in Table III. The disc used here was the same one used in the above experiment; its average thickness was 5.45 mm. Pressure was held constant throughout. Column IV, gives the time in minutes that the pressure was allowed to act.

TABLE III

I Pressure in kg	II Diameter in microns	III Number of bubbles	IV Time in minutes
8	0.369	None	1
8	0.369	1	1 ³ / ₄
8	0.369	10	2
8	0.369	30	2 ¹ / ₂
8	0.369	50	3
8	0.369	120	4
8	0.369	120	5
8	0.369	120	6
8	0.369	120	8

With this plate the least time for the appearance of the maximum number of bubbles was about four minutes.

The method employed to saturate the porcelain plates with the liquids, was to put the porcelain in a beaker of the liquid, then set the beaker under a bell jar and evacuate the jar by means of a Geryk pump. Under diminished pressure the air bubbles in the porcelain expand and the air comes out of the pores allowing them to fill with the liquids when subjected to atmospheric pressure again. This method is more satisfactory than attempting to drive out the air by forcing the liquid into the plate, for in the latter process air, held in recesses of the porcelain, becomes compressed and is not removed.

Results

Table IV contains some of the results obtained with different samples of porcelain.¹ P, represents the pressure

¹ Eighty-one different samples of porcelain were used in this series.

in kilograms per square centimeter and D, the diameter of the pores in microns.

TABLE IV—PORCELAIN

P	D	Osmotic effect
2.5	1.18	None
2.6	1.14	None
3.0	0.99	None
3.6	0.83	None
3.8	0.78	None
4.0	0.74	None
4.5	0.65	None
5.0	0.59	None
5.5	0.54	None
6.0	0.49	None
7.0	0.42	Possibly a slight effect
7.6	0.39	Surely some effect
8.0	0.37	More effect
8.5	0.35	Marked effect
9.0	0.33	Marked effect
15.0	0.19	Greatest effect

The results show that if the diameter of the pores is more than the 7 kilo value (0.42 microns) there is no osmotic effect, while if the diameter is less than this there is osmotic effect; also the smaller the pore diameter the greater the osmotic effect. Never less than three, and in some cases as many as ten, independent experiments were carried out with each grade of porcelain.

Method of Clogging Pores of Porcelain.—The porcelain discs used for the precipitation membranes had pore diameters of 1.18 microns and gave no osmotic effect when tested alone with normal sugar solution. Three distinct methods were used for clogging the pores of the porcelain. (1) A solution containing the finely divided precipitate was forced through with air pressure until sufficient clogging was effected. (2) The two solutions used for precipitation were placed on opposite sides of the disc, allowed to penetrate and form a precipitate at the point of meeting. (3) The disc was first saturated with one of the solutions then placed in the other

solution. The last method seemed to offer the best means to control the extent of clogging.

Barium Sulphate Precipitate in Porcelain.—Porcelain discs, of such coarse grain that when tested they gave no osmotic effects, were selected and their pores were clogged by precipitating barium sulphate within them. These plates were first saturated with an M/2 barium chloride solution under diminished pressure. They were then placed in a solution of sodium sulphate for some time, after which sodium sulphate solution was slowly forced through with air pressure. Water was forced through to remove the solutions present. The length of time, pressures employed, as also the concentrations of the solutions, were varied in order to obtain discs with varying degrees of porosity. Table V, contains results obtained with membranes of porcelain clogged with barium sulphate.

TABLE V—BARIUM SULPHATE

P	D	Osmotic effect
3.0	0.98	None
3.5	0.84	None
3.8	0.78	None
4.0	0.74	Slight effect
4.8	0.62	Slight effect
5.0	0.59	Marked effect
6.0	0.49	Marked effect
12.0	0.24	Marked effect

With this modified membrane the border line between osmotic effect and no osmotic effect is near the 4-kilo value (0.74 microns).

Sulphur Precipitate in Porcelain.—Porcelain plates of the same degree of porosity as those used in the preceding experiment, were clogged with a precipitate of sulphur. The plates were first saturated with a solution of sodium thio-sulphate by evacuation, then dilute sulphuric acid was forced through with air pressure, after which water was forced through to remove excess of both reagents. Also, in some of

the experiments, a solution containing finely divided sulphur was forced through in order to produce the clogging.

Table VI, contains some of the results obtained with these membranes.

TABLE VI—SULPHUR

P	D	Osmotic effect
3.2	0.93	None
4.0	0.74	None
4.5	0.66	None
5.0	0.59	Possibly a slight effect
6.0	0.49	Surely some effect
8.0	0.37	Marked effect
12.0	0.25	Marked effect
14.0	0.21	Marked effect
18.0	0.16	Marked effect

When the diameter of the pores was greater than that represented by the 5-kilo value (0.59 microns) no osmotic effect was obtained. In all cases when the diameter was less than this, osmotic effect was obtained.

Lead Chromate Precipitate in Porcelain.—The pores of coarse grained porcelain were clogged with a precipitate of lead chromate. The plates were first saturated with M/2 lead nitrate solution, under diminished pressure. They were next placed in an M/2 solution of potassium dichromate for a few minutes, then potassium dichromate solution was forced through the plate with air pressure. Water was forced through to remove excess of solutions. Table VII gives some of the results.

TABLE VII—LEAD CHROMATE

P	D	Osmotic effect
3.0	0.98	None
3.4	0.85	None
3.6	0.82	None
3.8	0.78	Possibly slight effect
4.0	0.74	Marked effect
4.2	0.72	Marked effect
4.4	0.68	Marked effect
5.0	0.59	Marked effect

Lead Sulphate Precipitate in Porcelain.—Porcelain discs were saturated with M/2 lead nitrate solution under diminished pressure. The discs were then placed in sodium sulphate solution for lengths of time varying from 5 seconds to 1¹/₂ hours. By varying the time in this manner it was possible to regulate the extent of clogging. The results of two series of experiments, together with the average osmotic effects of these are shown in Table VIII.

TABLE VIII—LEAD SULPHATE

No. exp.	P	D	Osmotic effect ¹ (24 hours)		
			Series I	Series II	Average
1	2.6	1.13	None	None	None
2	3.0	0.984	None	None	None
3	3.2	0.923	7	8	7.5
4	3.4	0.868	16	None	8
5	3.8	0.777	19	5	12
6	4.0	0.738	9	15	12
7	4.4	0.671	22 (109)	12	17
8	4.8	0.615	35	10	22.5
9	5.0	0.591	23	33	28
10	8.0	0.369	23	12	18
11	10.0	0.295	28	—	28

The cells were allowed to stand for several days. It was noted that the osmotic effects in experiments 1, 2, 3, 4, and 5 had reached a maximum at the end of 24 hours. None of the other membranes with somewhat smaller pore diameters showed a maximum at the end of this time. For example, at the end of eight days the cell in Experiment 7, showed a rise of 109 mm and had, apparently, not yet reached a maximum.

Copper Sulphide Precipitate in Porcelain.—To form the precipitate, porcelain discs, saturated with M/2 copper nitrate solution, were placed in ammonium sulphide solution for varying lengths of time. Table IX, contains results obtained in a single series with copper sulphide membranes.

¹ Osmotic effect is represented by the rise in mm of the sugar solution.

TABLE IX—COPPER SULPHIDE

P	D	Osmotic effect (48 hours)
3.2	0.92	None
3.4	0.86	None
3.6	0.82	None
4.0	0.73	1
4.2	0.70	3
4.4	0.67	2
4.8	0.61	18
5.4	0.54	4
5.6	0.52	8
5.8	0.50	11
6.0	0.49	16
6.4	0.46	7
7.2	0.41	19
7.4	0.40	14
8.0	0.37	16

Copper Ferrocyanide Precipitate in Porcelain.—Two distinct methods were used for precipitating copper ferrocyanide within the porcelain. In one series, the disc was saturated with M/2 copper nitrate solution, M/2 potassium ferrocyanide solution was then slowly forced through with air pressure, after which the two solutions were forced through alternately. Results obtained with these membranes are given in Table X, Series I. In the other series, solutions of lead nitrate and potassium ferrocyanide were placed on opposite sides of the membrane and allowed to penetrate and form a precipitate at the place of meeting. Results obtained by this method are given in Series II.

Corresponding results in the two series do not agree as closely as might be expected. This divergence is undoubtedly due to the difference in the methods employed in forming the precipitates.

In experiments with some of the so-called insoluble crystalline precipitates it was found that the precise treatment during the clogging of the pores has much to do with the magnitude of the osmotic effects obtained. Unfortunately, however, similar methods could not be used in all the experi-

TABLE X—COPPER FERROCYANIDE¹

P	D	Osmotic effect (24 hours)	
		Series I	Series II
2.8	1.05	None	None
3.0	0.98	None	—
3.2	0.92	None	4
3.4	0.86	None	45
3.5	0.84	—	9
3.6	0.82	None	12
4.0	0.73	5	—
4.2	0.70	24	52
4.4	0.67	7	—
6.0	0.49	—	42
8.2	0.36	—	58
16.0	0.18	90	—

ments for the various precipitates require different treatment in order that the clogging of the porcelain may be of approximately the same degree, *i. e.*, in order that we may obtain discs with 100–125 pores with diameters near the border line between osmotic effect and no osmotic effect.

It should be mentioned, also, that experiments have been carried out with some “insoluble” precipitates which have not been entirely successful owing to the fact that sufficient clogging could not be effected with the methods thus far employed. Among such precipitates may be mentioned calcium oxalate and silver chromate.

Calcium Oxalate.—Porcelain discs, with pore diameters of 1.18 microns, were treated with solutions of calcium chloride and ammonium oxalate using all the methods for clogging previously described. After many attempts the pore diameters were finally reduced to 0.74 microns. These membranes when tested gave no osmotic effect.

Silver Chromate.—Solutions of potassium dichromate and silver nitrate were used with the porcelain of the porosity mentioned in the preceding experiment. After repeated

¹ The blank spaces in Table X, indicate that no experiments were made with membranes of corresponding pore diameters.

attempts pore diameters of 0.82 microns were obtained. Attempts at further clogging were not successful. As was to be expected, these membranes failed to give apparent osmotic effects when tested.

A Comparison of Results

A comparison of the results obtained in this investigation is given in Table XI.

TABLE XI

Membrane	Border line	
	Pressure	Pore diameter
Porcelain	7.0	0.422
Porcelain and sulphur	5.0	0.591
Porcelain and BaSO ₄	4.0	0.738
Porcelain and PbCrO ₄	3.8	0.777
Porcelain and PbSO ₄	3.2	0.923
Porcelain and CuS	4.0	0.738
Porcelain and Cu ₂ Fe(CN) ₆	3.2	0.923

The border line between osmotic effect and no osmotic effect is not quite the same for the different membranes, however, the values are of the same order of magnitude and probably agree as closely as could be expected, for comparatively large errors are possible in determining the pressure at which 100-125 bubbles appear. Since these values are not the same it cannot be definitely stated that the nature of the substance makes no difference, but they are so nearly the same that the pore diameter seems to be one of the main factors in determining the appearance of osmotic phenomena. The success in finding within rather narrow limits a pore diameter which, if exceeded, unsuits the membrane for demonstrating osmotic effects does not preclude the following possibility. Perhaps it is only through the pores of molecular dimensions that pure water passes through to the solution while the solution as a whole is leaking outward through all larger pores. When the inflow equals the outflow no change in level is observed; when the inflow slightly exceeds the outflow a change in

level is observed. Perhaps what was measured in this investigation was the pore diameter at which the "leak" was just a little less than the osmotic effect.

Summary

The maximum pore diameter with which apparent osmotic effects can be obtained was determined with membranes of plain porcelain and membranes of porcelain clogged with insoluble precipitates. A definite area (1.54 sq. cm) was investigated in every case. It was found that when there were 100-125 pores in this area with diameters greater than 0.923 microns, no osmotic effects were obtained.

The border line between osmotic effect and no osmotic effect seems to be practically the same for membranes clogged with insoluble crystalline precipitates and for those clogged with the so-called "semipermeable" precipitates.

In conclusion, the writer wishes to express his gratitude to Professor S. L. Bigelow for his interest and advice throughout the progress of this investigation.

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THE PERMEABILITY OF PORCELAIN AND COPPER FERROCYANIDE MEMBRANES

BY F. E. BARTELL

The relation between the diameter of the pores of membranes and osmotic effects obtained with the same membranes has been under investigation in this laboratory for several years by S. L. Bigelow¹ and co-workers. Experiments have been carried out with membranes of porcelain, collodion, gold beaters skin and parchment paper. Water was forced through these membranes and the permeability was determined under various conditions of temperature and pressure. It was found that Poiseuille's laws for the passage of liquids through capillary tubes apply to the passage of water through the above-mentioned membranes.

Values representing an approximation to the absolute permeabilities of these membranes were obtained. The permeability was expressed in terms of the number of cubic millimeters which pass through one square centimeter of membrane in one minute. This method of expressing permeability values was adopted in the present investigation.

Contents of this Investigation

Pressures used by Bigelow ranged between 9.8 mm and 834 mm of mercury. The work of Bigelow was repeated and verified, then extended through a much wider range of pressure. Pressures as high as 5885.7 mm of mercury were employed. The influence of temperature on the permeability of porcelain was also more fully investigated.

The permeability of copper ferrocyanide membranes, so much used in experimental studies of maximum osmotic pressures, was likewise determined. The permeability of these membranes, precipitated electrolytically in porcelain, was determined with temperature constant and with pressures varied between 58.6 mm and 2957.9 mm of mercury; also

¹ Jour. Am. Chem. Soc., 29, 1675 (1907).

with pressure constant and temperature varied between 20.5° and 65.5° C.

Apparatus

The apparatus used in the permeability determinations was a modification of that used by Bigelow and is illustrated in Fig. 1.

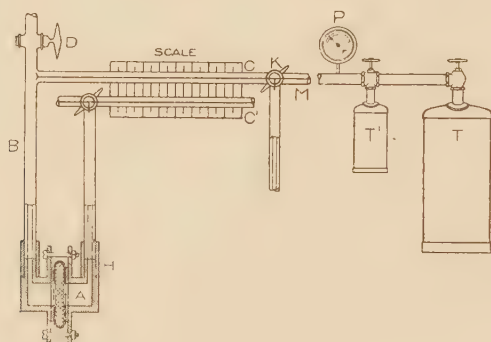


Fig. 1

The membrane which was to be studied, was placed between washers of rubber in the brass holder, H, which was tightened by means of three screws. The brass tube on one side of the holder was attached to a perpendicular glass tube, B, which was in turn sealed to the capillary tube C. This tube had been calibrated with mercury, and was used to measure the volume of water passing into the membrane. The brass tube on the other side of the holder was connected to the capillary tube C', the outlet tube, which had also been calibrated with mercury. Tap D served to introduce the water to be used. Stopcock K served the double purpose of admitting air pressure to bear on the water column in C and of releasing the pressure at the close of the experiment. A small gas tank, T, such as is used for transporting oxygen, contained compressed air, and from this tank pressures could be applied as desired. Pressures were read directly from the pressure gauge, P. To diminish the decrease in pressure, due to the small change in volume, caused by the movement of the meniscus in the capillary tube, tank T', was placed in con-

nection and served as an air chamber; with this arrangement there was no appreciable change in pressure during an experiment. When working with low pressures, the pressure tanks, T and T', were disconnected from the apparatus and in their stead mercury pressure bulbs were used. These bulbs were of good size, each having a capacity of about 250 cc. The lower bulb was attached directly to the air inlet tube, M. The other bulb, used to adjust the mercury pressure, was raised and lowered by means of a pulley and cord. A millimeter scale was placed in a perpendicular position between these bulbs, from this, readings were made by means of a cathetometer. The air space above the mercury, in the fixed bulb, was so large that the change of pressure during a single experiment was negligible.

Method of Measurement

The membrane holder was placed in water contained in a large beaker which was wrapped with layers of felt and asbestos. In this way the temperature was held constant, during an experiment, within half a degree. The tube B, was filled with distilled water by means of a capillary funnel, after which stopcock K was opened allowing the water to flow into the calibrated tube C. When the meniscus had reached the end of the scale, stopcocks D and K, were closed. The desired pressure was then applied, after which stopcock K was quickly opened allowing the pressure to bear on the water column. The water was forced through the membrane and out through the second capillary tube. By noting the distance over which the meniscus traveled in each tube along the millimeter scale, the volume of water passing into the membrane, and the volume coming through the membrane could be determined. By comparing these volumes it was possible to tell whether or not any leakage had occurred. The time for the meniscus to travel over a certain number of millimeters was noted by means of a stop watch. Usually the meniscus traveled over a distance of 50 mm. This represented a volume of 271.7 mm³ (with the outlet tube this distance represented a volume

of 201.2 mm³). The area of the membrane exposed was 1.767 cm².

Porcelain Membranes

Porcelain discs were cut from unglazed porcelain plates and ground, by means of emery paper, until they were about 4.5 mm in thickness and 30 mm in diameter. It was found that the amount of water which came through the membrane, and which was measured by means of the calibrated outlet tube, was considerably less than the amount forced into the membrane holder. This loss was due to leakage through pores which extended out to the edge of the porcelain disc. To diminish this leak the discs were coated with a layer of glaze¹ leaving uncovered only the central portion, about 15 mm in diameter.

Results with Porcelain

Temperature Constant, Pressure Varied.—Poiseuille's formula² for the passage of liquids through capillary tubes is: $Q = K \frac{P}{L} D^4 T$. Q , represents the volume of liquid passing through a capillary tube of length L , in time, T . P , represents the pressure, D , the diameter, and K , represents a constant for a definite temperature.

According to this formula, the volume of liquid passing in unit time is directly proportional to the pressure.

Table I, contains results obtained by forcing water through porcelain at different pressures, the temperature remaining constant.

¹ A low melting glaze, consisting of PbO, 78 parts; CaCO₃, 10.3 parts; Al₂O₃, 7.1 parts; SiO₂, 42 parts, was used. A small amount of CoO was added to give it a color. The mixture was first fused, ground to a fine powder, then mixed thoroughly with glycerine. The glycerine mixture proved more satisfactory than the ordinary mixture of glazing material and water. The discs were heated in a muffle furnace until the glaze was thoroughly melted. They were then allowed to cool slowly. By this method a number of discs were prepared which were free from cracks, and which showed no measurable loss by leakage under the pressures used.

² Chwolson: "Lehrbuch der Physik," Vol. I, p. 659 (1902).

TABLE I

Column I. Pressures in millimeters of mercury.
 Column II. The number of cubic millimeters of water passing through the membrane (represented by A).
 Column III. Time in seconds for the quantity, A, to pass through.
 Column IV. Number of cubic millimeters which pass through one square centimeter of membrane in one minute (represented by Q).
 Column V. Quotient obtained by dividing the Q values by the pressure, P.

I	II	III	IV	V
P	A	T	Q	$\frac{Q}{P}$
200	271.7	87.3	105.7	0.528
300	271.7	60.2	153.3	0.511
400	271.7	45.3	203.7	0.509
500	271.7	36.9	250.1	0.500
600	271.7	31.0	297.7	0.496
700	271.7	26.9	343.0	0.490

The temperature was maintained at 21.5° and did not vary more than 0.2° either way. The average thickness of the plate, measured by means of a micrometer caliper, was 3.84 mm, the thinnest portion 3.82 mm and the thickest 3.86 mm.

From the above results it is clear that the amount of water passing in unit time is very nearly proportional to the pressure. If the amount passing were exactly proportional to the pressure, the $\frac{Q}{P}$ values would be constant and this would mean that Poiseuille's formula for the passage of liquids through capillary tubes applies rigidly to the passage of water through porcelain. But these values, although nearly constant, do show a slight decrease with each successive determination.

To determine whether the decrease in permeability is merely a question of the time during which the experiment is running, of quantity of water passing through, perhaps of clogging of pores with solid particles, pressures were decreased in steps at definite time intervals and then, without stopping,

increased again through the same steps at the same time intervals. The results are given in Table II.

TABLE II

	P	A	T	Q	$\frac{Q}{P}$
1	400	201.2	60.4	113.2	0.2828
2	353	201.2	68.9	99.2	0.2809
3	297	201.2	83.2	82.1	0.2765
4	146	201.2	170.6	40.0	0.2745
5	53	201.2	474.0	14.4	0.2719
6	53	201.2	476.0	14.3	0.2708
7	146	201.2	173.6	39.4	0.2696
8	297	201.2	86.0	79.4	0.2674
9	353	201.2	73.8	92.5	0.2622
10	400	201.2	65.5	104.3	0.2608

Table III, contains the arithmetical mean of the two determinations at each pressure.

TABLE III

	P	A	T	Q	$\frac{Q}{P}$
1	53	201.2	475.0	14.35	0.2714
2	146	201.2	172.1	39.7	0.2720
3	297	201.2	84.6	80.7	0.2719
4	353	201.2	71.3	95.8	0.2714
5	400	201.2	62.9	108.7	0.2717

These results represent the mean permeability during an experiment and show an admirable constancy for the value of $\frac{Q}{P}$ *i. e.*, the amount passing is directly proportional to the pressure and Poiseuille's formula does apply.

The decrease in permeability must be attributed to one of two causes; either the porcelain undergoes some change in nature or the pores become clogged with insoluble material. By forcing water through the disc in the direction opposed to that in which it had passed during the experiment, and

brushing the surface with a fine stiff brush, the porcelain was put in such condition that it once more gave practically the same values as at the beginning. Freshly distilled water was used so that it hardly seemed possible that the clogging was due to impurities originally present in the water.

Bede¹ and Wilhelmy,² by different methods, arrived at the conclusion that the liquid layer in contact with a solid surface is less mobile than the remainder of the liquid. Duclaux³ makes use of this conclusion and ascribes the decrease in permeability of membranes with continued passage of water, as due to the gradual thickening of the layer of the less mobile liquid on the walls of the capillary pores. The results of Bigelow's experiments show that the membranes of collodion and gold beaters skin do not show a similar decrease. This fact, together with the results mentioned above, makes Duclaux's theory improbable. Schmidt noted a change in permeability with continued passage of water through membranes. He ascribed a decrease in permeability to the clogging of the pores with solid particles. In his investigations he observed every precaution to remove impurities from the distilled water used. Quincke,⁴ also obtained permeability results showing a decrease with continued passage of water. He was led to conclude that small particles were mechanically broken off the membrane and carried into the pores.

It seems that the most logical explanation of the decrease in permeability in the present investigation is that expressed by Quincke; *i. e.*, the gradual decrease in permeability of the porcelain membranes is due to clogging by small particles of porcelain which are mechanically broken off the plate and carried, by the water, into the capillary pores.

Since efforts to eliminate the trouble were unsuccessful the system of averaging, above described, was used in Tables

¹ Bull. Acad. Belg., [2] 10, 47-55 (1860).

² Pogg. Ann., 122, 9 (1864).

³ Ann. Chim. Phys., 25, 433-501 (1872).

⁴ Pogg. Ann., 107, 21 (1859).

IV and V. In each of these tables temperature was held constant and pressures were varied.¹

TABLE IV

P	A	T	Q	$\frac{Q}{P}$
76.7	40.24	160.1	8.53	0.1113
118.3	40.24	103.1	13.20	0.1120
228.7	40.24	53.8	25.40	0.1110
322.2	40.24	37.9	36.06	0.1119
405.3	40.24	30.1	45.39	0.1121
516.7	40.24	23.8	57.41	0.1111
622.9	40.24	19.7	69.36	0.1113
709.2	40.24	17.3	79.00	0.1114
827.8	40.24	14.9	91.70	0.1108
935.7	40.24	13.1	104.3	0.1115

Thickness of plate, 4.5 mm.

Temperature, 21.4°.

TABLE V

P	A	T	Q	$\frac{Q}{P}$
1471.4	543.4	27.4	673.5	0.457
2207.1	543.4	18.4	1003.3	0.454
2942.8	543.4	14.0	1318.3	0.447
3678.6	543.4	11.3	1632.7	0.444
4414.2	543.4	9.3	1984.5	0.449
5150.0	543.4	7.9	2336.2	0.453
5885.7	543.4	6.9	2674.8	0.454

Thickness of plate, 4.5 mm.²

Temperature, 22°.

In the experiments with both low and high pressures, when corrections are made for the gradual decrease in permeability, we obtain, very nearly, a direct proportionality between the amount passing in unit time and the pressure.

¹ Pressures in Table IV were obtained with mercury pressure bulbs. Pressures in Table V were read directly from the pressure gauge and were converted to mercury pressures.

² The thickness of the plate was the same as in the previous experiment but the porcelain was of a different grade.

Pressure Constant, Temperature Varied.—In Poiseuille's formula $Q = \frac{K P D^4 T}{L}$, K , represents a constant for a definite temperature. The formula to express the variation of K , with temperature is: $K = K_0 (1 + 0.03368t + 0.000221t^2)$.¹

In the present investigation, P and T (time) were held constant, and we will assume that D and L remain constant, we have then $\frac{P D^4 T}{L} = \text{a constant, } C$, which gives $Q = KC$. Substituting in the temperature equation we obtain

$$\frac{Q}{1 + 0.03368t + 0.000221t^2} = K_0 C.$$

Having obtained the values for Q , T (time) and t (temperature) we can calculate the values for $K_0 C$.

If Poiseuille's laws for the passage of liquids through capillary tubes apply to the passage of water through the membranes studied, we should get a constant value for $K_0 C$.

Table VI, contains results obtained by forcing water through porcelain at constant pressure but at different temperatures.

TABLE VI

Column I. Pressures in millimeters of mercury.

Column II. Number of millimeters per minute meniscus traveled in calibrated tube.

Column III. Temperature.

Column IV. Number of cubic millimeters which pass through one square centimeter of membrane in one minute.

Column V. $K_0 C$ values.

P	mm. per min.	t	Q	$K_0 C$
650	89.09	18	273.8	163.2
650	109.5	28	336.7	159.2
650	133.3	38	410.1	157.8
650	158.7	48	488.2	156.2
650	186.3	58	573.1	155.1
650	199.6	68	659.1	152.9
650	243.9	78	750.2	150.9

Thickness of plate, 3.94 mm.

¹ Chwolson: "Lehrbuch der Physik,," Vol. I, p. 659.

The values for K_oC should remain constant throughout the experiment for P and T were held constant in every case. The values are not constant; with each successive determination there is a slight decrease in the K_oC values which shows that there must be a smaller increase in the Q values with increase in temperature than should occur if Poiseuille's formula applies. These results are analogous to those obtained by Bigelow and are also similar to those obtained in Tables I and II. No allowance was made for clogging of pores.

Table VII, was obtained with still a different plate. Results at each pressure represent the average of six determinations. The system of averaging used in the pressure experiments, was employed.

TABLE VII

P	mm. per min.	<i>t</i>	Q	K_oC
696.4	61.5	22.1	140.0	77.43
697.5	78.7	32.0	179.3	78.16
697.0	93.5	41.3	212.8	76.86
693.5	113.2	52.1	257.8	76.88
695.0	135.1	61.9	307.0	77.89
694.5	150.0	70.0	340.8	76.74

Thickness of plate, 4.5 mm.

The values for K_oC thus obtained show a fairly close agreement. When corrections are made for differences in pressure the values obtained are still more nearly constant as is noted in Table VIII. Q^p represents the quantity which would have passed had the pressure been held constant at 693.5 mm. K_oC' represents the new values calculated from the Q^p values. These values are, in all probability, constant within the limits of experimental error.

TABLE VIII

t	P	P'	Q	Q ^P	K ₀ C'
22.1	696.4	693.5	140.0	139.4	77.11
32.0	697.5	693.5	179.3	178.2	77.54
41.3	697.0	693.5	212.8	211.6	76.47
52.1	693.5	693.5	257.8	257.8	76.88
61.9	695.0	693.5	307.0	306.3	77.80
70.0	694.5	693.5	340.8	340.2	76.63

The change of permeability with change of temperature is in reality a measure of the change of the viscosity of the water due to this change in temperature. Poiseuille's viscosity formula is $\eta = \frac{\pi P R^4}{8 Q L} T^1$ (η represents the coefficient of viscosity). The pressure required to force a liquid through a capillary tube is directly proportional to the viscosity of the liquid, while the amount coming through, per unit of time, at any given pressure, is inversely proportional to the viscosity, *i. e.* $\eta'/\eta = Q/Q'$. Viscosity values calculated from the results in Table VIII, are given below in Column III of Table IX. These results were obtained by using the formula $\eta' = \frac{\eta Q}{Q'}$. As a basis for calculation, the values $\eta = 0.00957$ and $Q = 139.4$ were used.

An empirical formula for the calculation of viscosity at any temperature is: $\eta^t = \frac{\eta_0}{1 + at + bt^2}$. For water, $a = 0.0332$, $b = 0.000244$, and $\eta_0 = 1.775$.² Values representing the viscosity of water, at the temperatures employed in this experiment, were calculated by this formula and are given in Column IV.

¹ Chwolson: Vol. I, p. 643.

² Chwolson: Vol. I, p. 648.

TABLE IX

I t	II Q^p	III $\eta' = \frac{\eta Q}{Q'}$	IV $\eta^t = \frac{\eta^o}{1 + at + bt^2}$
22.1	139.4	0.00957	0.00957
32.0	178.2	0.00747	0.00767
41.3	211.6	0.00630	0.00636
52.1	257.8	0.00518	0.00523
61.9	306.3	0.00436	0.00444
70.0	340.2	0.00392	0.00393

From these results it is apparent that a measurement of the change of permeability at different temperatures, pressure constant, is nothing more or less than a measure of the change of the viscosity of the liquid. It then follows, that if we know the amount of liquid which passes through a membrane in unit time, at a given temperature and pressure, we can readily calculate that amount which would pass through at any other temperature, $Q' = \frac{Q\eta}{\eta'}$.

Permeability of Copper Ferrocyanide

Pfeffer,¹ gives some permeability values obtained by forcing water through copper ferrocyanide membranes. He used pressures varying between 37.8 and 210.2 cm of mercury. His results are few and he gives only the pressures and the quotient obtained by dividing the amount of water passing through in unit time by the corresponding pressure. They indicate, however, a direct proportionality between the amount of water passing through in unit time and the pressure.

Sebor,² deposited a copper ferrocyanide membrane in a Pukall porcelain cup. He gives the results of one series of six observations, obtained at 18°, with pressures varying between 4 and 23.2 cm of water; the results obtained show a direct proportionality between the time and the pressure. He prepared a similar Pukall cell, precipitating the copper

¹ Osmotische Untersuchungen, Leipzig, pp. 70-72 (1877).

² Zeit. Electrochemie, 10, 347-53 (1904).

ferrocyanide membrane by the electrolytic method of Morse.¹ By a test in which low pressures were used, he found that practically no water passed through the cell in 24 hours. No experiments were made with higher pressures.

Preparation of Copper Ferrocyanide Membranes

Copper ferrocyanide was precipitated, by the electrolytic method, within glazed porcelain discs similar to those used in the preceding experiments.

During the precipitation of the membrane, the plate A, was placed vertically between two glass cylinders, C and C', each 40 mm in length and 30 mm in diameter with washers of rubber B and B', between the ends of the cylinders and the porcelain. Into the other end of each cylinder was inserted a three-hole rubber stopper; in the upper holes were inlet tubes, D and D', used for supplying the solutions; in the lower holes were placed the outlet tubes, F and F', for the removal

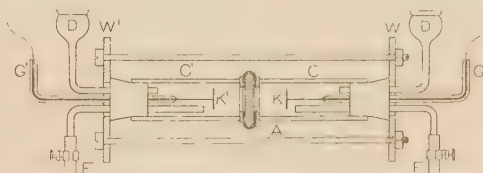


Fig. 2

of the alkaline solution formed during the precipitation; while through the remaining holes were inserted the connections carrying the electrodes K and K', which were placed about 2.5 cm from the porcelain plate. Bearing on the ends of the rubber stoppers were two iron washers, W and W', held by three screws with which pressure could be applied to keep the apparatus together.

The method for the removal of the air from the plate, as also the method for the deposition of the membrane, was practically the same as that used by Morse and Horn.²

¹ Morse and Horn: *Am. Chem. Jour.*, 26, 80-86 (1901).

² *Loc. cit.*

The precipitation was continued until a resistance of 400,000 ohms was obtained.

Results with Copper Ferrocyanide

The apparatus and method for the determination of the permeability of copper ferrocyanide membranes was the same as that used in the experiments with porcelain. The system of averaging results was not employed.

In the pressure experiments the temperature was maintained at 22° and did not vary more than 0.2° either way.

The values in Table X, were obtained with temperature constant and pressure varied.

TABLE X

P	A	T	Q	$\frac{Q}{P}$
588.5	54.35	720	2.56	0.00434
883.0	54.35	490	3.76	0.00426
1177.3	54.35	375	4.92	0.00417
1471.6	54.35	300	6.15	0.00418
1839.5	54.35	232	7.95	0.00439
2207.4	54.35	195	9.46	0.00428
2575.3	54.35	167	11.05	0.00429
2957.9	54.35	145	12.73	0.00430

The permeability values obtained with copper ferrocyanide are very much less than those obtained with porcelain but there is, however, the same direct proportionality between the amount of water passing and the pressure.

Table XI, contains results with pressure constant and temperature varied.

TABLE XI

P	mm. per min.	t	Q	K ₀ C
2207	6.74	65.5	20.73	4.938
2207	6.13	61.0	18.86	4.873
2207	5.40	53.0	16.62	4.885
2207	4.63	46.5	14.24	4.650
2207	2.86	20.5	8.79	4.935

In the experiments with both the porcelain and the copper ferrocyanide membranes values were obtained for $\frac{Q}{P}$ indicating that the amount of water passing was directly proportional to the pressure, also constant values were obtained for K_0C . It seems, therefore, that we are justified in concluding that *Poiseuille's laws for the passage of liquids through capillary tubes apply to the passage of water through porcelain and through copper ferrocyanide membranes.*

The fact that Poiseuille's laws apply to the passage of water through porcelain and copper ferrocyanide membranes is strong evidence in favor of the theory that these membranes are capillary in structure, though it is by no means conclusive proof of such structure. It is not difficult to conceive of a capillary structure in porcelain, but in the case of copper ferrocyanide the interstices are much smaller, they are in all probability within the region of molecular dimensions. These results, then, are in accordance with the conclusions reached by Bigelow from his work with collodion membranes, that "the rate of passage of liquids through molecular interstices is expressible by the same laws which formulate the rate of passage of liquids through capillary tubes." Furthermore, it seems improbable that we shall ever be able to differentiate, experimentally, between the region of so-called capillary spaces and the region of intramolecular spaces.

Summary of Results

In this investigation it is shown that the decrease in the permeability of porcelain, during the passage of water, is due to mechanical clogging of the pores. However, constant permeability values were obtained by employing a system of averaging results.

It is demonstrated experimentally that Poiseuille's laws for the passage of liquids through capillary tubes apply to the passage of water through unglazed porcelain from pressures of 53 mm of mercury to pressures of 5885.7 mm of mercury.

Poiseuille's formulation for the passage of liquids through

capillary tubes as influenced by change of temperature, is found to apply to the passage of water through porcelain from 22.8–70° C.

Poiseuille's laws, as expressing both pressure and temperature variations, were found to apply to the passage of water through electrolytically precipitated membranes of copper ferrocyanide in porcelain.

In conclusion, I desire to express my thanks to Professor S. L. Bigelow for the original suggestion and for his advice and interest throughout the work.

*University of Michigan,
April, 1911*

